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Dear Kendra,

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4. TITLE: In situ monitoring of thermal transitions in thin polymeric films via optical interferometry
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Thanks,

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In situ monitoring of thermal transitions in thin polymeric films via optical interferometry

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Abstract

A novel, low-cost, rapid, accurate, non-invasive and high throughput method based on the principles of *Optical Interferometry* (OPTI method) has been developed and applied for the in situ monitoring in one simple run of first (melting) and second (glass transition) order transitions as well as of the thermally induced decomposition of various thin polymeric films spin coated on flat reflective substrates (untreated silicon wafers). The new method has been applied successfully for measuring the glass transition, melting and decomposition temperatures of six commercially available polymers [poly(methyl methacrylate) (PMMA), poly(2-hydroxyethyl methacrylate), (PHEMA), poly(vinyl acetate-*co*-crotonic acid), (PVACA), poly(vinyl pyrrolidone) (PVP), poly(vinyl chloride-*co*-vinyl acetate) (PVCVA) and crystalline poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVFHP)] of known T_g s or T_m s. The recorded interferometric signals were identified and characteristic signal patterns were qualitatively correlated to specific transitions. The monitoring of first and second order transitions in thin polymeric films is based on detectable differentiations of the total energy of a fixed wavelength laser beam incident almost vertically (angle of incidence $<5^\circ$) onto a thin polymeric film spin coated on a flat reflective substrate. These differentiations are caused by film thickness and/or refractive index changes of the polymeric film both resulted from the significant change of the polymer's free volume taking place on the transitions. For film thicknesses over approx. 200–250 nm, the T_g or T_m of the polymeric films measured with the OPTI method were in excellent agreement with the corresponding values of the polymer, measured by DSC. An investigation on the trends of the T_g of PHEMA and PMMA films in a wide thickness range (30–1735 nm) was also carried out. Ultra-thin (~ 30 nm) films of PMMA and PHEMA showed significant increase in their T_g values by approx. 30 °C upon comparing to their corresponding bulk T_g s. This behavior was attributed to an enhanced polymer–surface interaction through hydrogen bonding and/or to changes in the tacticity of the polymer.

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Keywords: Glass transition temperature; Optical interferometry; Thin films

1. Introduction

Nowadays polymer-based materials are becoming ubiquitous in a variety of high-tech applications, e.g. specialty coatings, automotive, aerospace, semiconductors, composites, optics, etc. The involvement of polymers in modern technological processes is unique and indispensable to the evolution of advanced products. A constantly increasing use of polymer-based materials has highlighted the need for a better understanding of their physical, chemical and mechanical properties. More specifically, the understanding of the principles and the mechanisms through which the performance of polymeric materials can be controlled and fine tuned according to the requirements of a specific

application has fairly received a great technological importance and consequently still attracts world research interest.

The thermal properties of a polymer, e.g. glass transition, melting/crystallization, and decomposition temperature, are characteristics that specify up to a significant extent its physical properties and processability, consequently, potential technological applications. The understanding of the parameters that may affect the physical properties of materials or devices containing thin polymeric films or high performance polymer–inorganic interfaces has attracted the interest of various scientific communities and is related to many modern and emerging technologies in, e.g. semiconductor industry (photoresists for microlithography and polymers as low- K dielectrics, etc.), microsystems, nanotechnology, biocompatible materials (development of human artificial tissues), pharmaceuticals (new drugs with controlled release features).

The nature of the physical transitions of polymers from

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liquid to glass and the dynamics of molecular motion in glassy systems are active areas of research [1]. Up to today, a great deal of progress has been made in developing new and accurate methods for measuring thermal transitions (especially the glass transition and melting/crystallization) of polymers [2–4] and/or polymer-based materials. Methods and techniques include the: modulate differential scanning calorimetry (MDSC), dynamic mechanical analysis (DMA), thermal mechanical analysis (TMA), dilatometry, positron annihilation spectroscopy (PALS) [5], scanning viscoelasticity microscopy (SVM) [6], X-ray reflectivity [7], quartz crystal microbalance (QCM) [8], spectroscopic [9] and nulling ellipsometry [10], local thermal analysis [11], fluorescence [12], electrical conductivity [13] along with viscosity measurements and Brillouin light scattering [14]. These techniques are used by materials science experts across all fields, where polymers meet modern needs for advanced materials. Certain of the aforementioned techniques have already been applied in monitoring the glass transition and/or the melting/crystallization in thin polymeric films, e.g. ellipsometry and thin-film DSC [15].

Although, the behavior of polymeric molecules in the bulk is essentially known, this is not the case for macromolecules near interfaces. The significant surface/volume ratios present in ultra-thin polymeric films make them highly interfacial in nature. On an average, each macromolecular constituent of such system is in contact with an interface, either the solid substrate or the free surface. In the most extreme cases, each macromolecule could be confined between a solid interface and the free surface. Consequently, there are two main factors that differentiate macromolecules in ultra-thin polymeric films from those present in the bulk: confinement and substrate interactions. It should be noted that regardless of the polymer's film thickness, there is an interface near the solid substrate, where the physical properties are expected to be significantly different to those of the bulk material.

As mentioned earlier, many high performance materials and devices contain polymer–inorganic interfaces and despite their great technological importance, the properties of these interfaces are not well understood experimentally or theoretically [16,17]. This is unfortunate since the interfacial properties often determine the performance of these materials and devices. The microscopic interface properties are intimately related to the macroscopic phenomena of adhesion and debonding. Our present study aims to introduce a novel, rapid (one simple run is required), non-invasive method, based on the principles of optical interferometry [18] [OPTI (OPTical Interferometry)], for measuring with accuracy in thin and ultra-thin polymeric films certain phase transitions [melting (first order transition), glass transition (second order transition)] as well as thermal decomposition. This study hopes to promote further the investigation on the interfacial properties of ultra-thin polymeric films that undoubtedly attract world research

interest and enjoy wide acceptability in advanced technological applications.

2. Experimental section

Poly(methyl methacrylate) (PMMA) [$M_w = 120,000$, $T_g = 114^\circ\text{C}$ (DSC)] and poly(vinyl acetate-*co*-crotonic acid) (PVACA) [$M_n = 27,000$, $T_g = 61^\circ\text{C}$ (DSC, onset), crotonic acid content 10 mol%], poly(vinyl pyrrolidone) (PVP) [$M_w = 160,000$, $T_g = 142^\circ\text{C}$ (DSC, onset)], poly(2-hydroxyethyl methacrylate) (PHEMA) [$M_v = 300,000$, $T_g = 55^\circ\text{C}$ (DSC)], poly(vinyl chloride-*co*-vinyl acetate) (PVCVA) [$M_n = 27,000$, $T_g = 72^\circ\text{C}$ (DSC), vinyl acetate content 14 wt%], poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVFHP) [$M_w = 400,000$, $M_n = 130,000$, $T_g = -40^\circ\text{C}$ (DSC) and $T_m = 140\text{--}145^\circ\text{C}$ (DSC)], *N*-methyl-pyrrolidone (NMP), *N,N'*-dimethyl formamide (DMF) and propylene glycol methyl ether acetate (PGMEA) and ethyl(S)-(-)-lactate (EL) were purchased from the Aldrich Chemical Company and used as supplied. The DSC data of the polymers were provided by the Aldrich Chemical Company.

Solutions of 1.0, 2.5, 5.0, 8.0, 12.0% (w/w) PMMA in PGMEA and 1.0 and 8.0% (w/w) in toluene, 1.0, 3.0, 7.0, 12.0% (w/w) PHEMA in EL, 5% (w/w) PVACA in NMP, 5% (w/w) PVP in DMF, 5% (w/w) PVCVA in NMP, and 5% (w/w) PVFHP in NMP, were prepared upon overnight stirring and, where necessary slight heating (up to 50°C) was applied. Films of various thicknesses of the aforementioned polymers were obtained upon spin coating the aforementioned solutions on untreated silicon substrates (silicon wafers, $30 \times 30\text{ mm}$) (Table 1). Subsequently, the samples (silicon wafers coated with a polymeric film) were placed into a vacuum oven at 120°C and were baked for 1 h, in order to remove any remaining solvent traces. The process of the PVFHP films involved vacuum baking at 100°C for 1 h. Film thickness measurements were performed on a Dektakla profilometer. The sample polymeric films were named after their polymer and a number corresponding to their film thickness in nanometers.

For the in situ measurement of the glass transition, melting and thermal decomposition of all the aforementioned thin polymeric films (T_g^{film} , T_m^{film} and $T_{\text{dec}}^{\text{film}}$, respectively) an experimental optical interferometry apparatus has been developed. It consisted of a hot plate equipped with a digital temperature controller [acc. $\pm 0.5^\circ\text{C}$, heating rate of $15^\circ\text{C}/\text{min}$ (air atmosphere)], a diode laser beam source at 650 nm (fixed wavelength) properly mounted and leveled on the hot plate and a data acquisition card (DAC) with 12 bits resolution and satisfactory sampling rate capability was used for monitoring the voltage. The DAC monitored simultaneously the hot plate's temperature and the total energy incident on a properly mounted detector, which was equipped with a narrow band filter in order to eliminate the effect of ambient light on the signal acquired.

Table 1

The PMMA, PHEMA, PVP, PVACA, PVCVA and PVFHP films preparation and their corresponding thicknesses and names

Polymers	Solvent	Solution concentration (w/w%)	Spin coating speed (rpm)	Thickness (nm)	Sample film
PMMA	PGMEA	1.0	1000	30	PMMA ₃₀
	PGMEA	2.5	4500	42	PMMA ₄₂
	PGMEA	2.5	1000	88	PMMA ₈₈
	PGMEA	5.0	4500	110	PMMA ₁₁₀
	PGMEA	8.0	4500	235	PMMA ₂₃₅
	PGMEA	8.0	1000	440	PMMA ₄₄₀
	PGMEA	12.0	4500	585	PMMA ₅₈₅
	PGMEA	12.0	1000	1235	PMMA ₁₂₃₅
	Toluene	1.0	1000	30	PMMA _{30T}
	Toluene	8.0	1000	440	PMMA _{440T}
PHEMA	EL	1.0	1000	32	PHEMA ₃₂
	EL	3.0	7000	55	PHEMA ₅₅
	EL	3.0	4500	65	PHEMA ₆₅
	EL	3.0	1000	135	PHEMA ₁₃₅
	EL	7.0	4500	255	PHEMA ₂₅₅
	EL	7.0	1000	585	PHEMA ₅₈₅
	EL	12.0	4500	720	PHEMA ₇₂₀
	EL	12.0	1000	1735	PHEMA ₁₇₃₅
PVP	DMF	5.0	1000	190	PVP ₁₉₀
PVACA	NMP	5.0	1000	300	PVACA ₃₀₀
PVCVA	NMP	5.0	4500	465	PVCVA ₄₆₅
PVFHP	NMP	5.0	1000	430	PVFHP ₄₃₀

The interferograms (interferometric signal vs. temperature) presented here after, are recorded in a simple run the total duration of which is only determined by the heating rate applied for the measurement.

3. Results and discussion

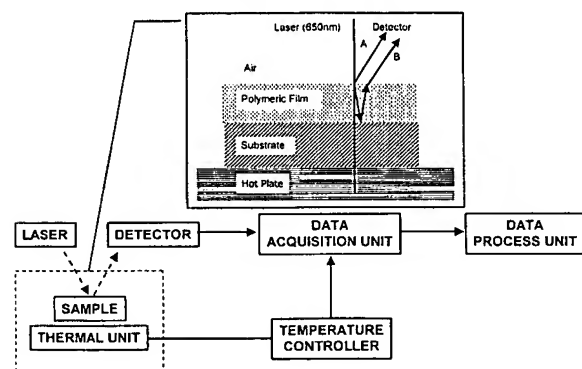
3.1. Principles and experimental set up of the OPTI method (Scheme 1)

Interferometry has been proved to be a precise and straightforward technique for studying certain interesting phenomena in various research fields (physics, astronomy, microelectronics, etc.) and its applications in materials science is of great importance when a better insight in

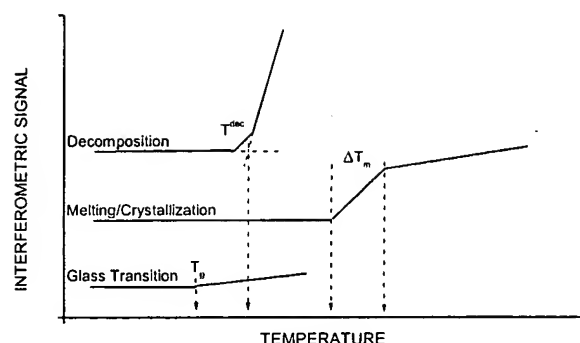
phenomena that take place mainly in interfaces, is the subject of the research.

In the present study we report a novel, rapid, non-invasive method based on the principles of optical interferometry (OPTI method), for the in situ monitoring of first and second order transitions as well as thermally induced decomposition of certain thin and ultra-thin polymeric films (see Section 2) spin-coated on flat reflective substrates (untreated silicon wafers).

Scheme 1 presents the experimental set up of the OPTI method along with the data flow and process. The OPTI device consists of a laser source, a detector, a data acquisition card, a data process unit, a thermal unit equipped with a temperature controller and the sample (thin polymeric film) spin coated on a reflective substrate (e.g. silicon wafer). In an advanced version of the set up used in the present study and depicted in Scheme 1, a cooling device can be incorporated for measuring transitions that take place at temperatures lower than room temperature. It should be also stressed that the laser's wavelength must be carefully selected to be such, where the sample is transparent (negligible absorptivity). Theoretically this is a potential limitation of the method but nowadays laser sources are commercially available in a vast variety of different wavelengths and consequently this theoretical limitation imposes no practical difficulties to the method. On the contrary, the fact that commercially available lasers emitting at various wavelengths are widely supplied, offers to the user the possibility not only to adjust its set up in a way to meet the sample's necessary transparency requirement but also to fine tune the resolution of the system according to the demands of the analysis.



Scheme 1. Schematic of the OPTI experimental set up and data flow.



Scheme 2. Schematic representation of a typical interferogram representing first and second order transitions as well as thermally induced decomposition. The diagram can be used as a generic guide for the interpretation of the thin polymeric films' interferometric signal.

The laser emission wavelength we selected for our studies was at 650 nm, where the absorption of our spin-coated polymers is negligible, if not nilpotent. The sample is placed on the hot plate and the light beam from the laser source incidents almost vertically (angle of incident $< 5^\circ$) on the polymeric film surface. Both the wavelength of the laser source and the angle of incident are fixed. Due to refractive index transitions at the air-polymeric film and polymeric film–substrate interfaces, multiple reflections within the polymeric film occur. The total energy incident on the detector could be approximated as the sum of the energy from two beams. One beam (A) comes from the polymeric film surface and the second (B) from the polymeric film–silicon substrate interface (Scheme 1). The total energy E that incidents on the detector could be approximated as

$$E = A_0^2 + B_0^2 + 2A_0B_0 \cos\left(\frac{4\pi n_1}{\lambda} d_f\right) \quad (1)$$

where A_0 is the amplitude of beam A, B_0 the amplitude of beam B, n_1 the refractive index of the thin polymeric film, λ the laser's wavelength and d_f the thickness of the polymeric film.

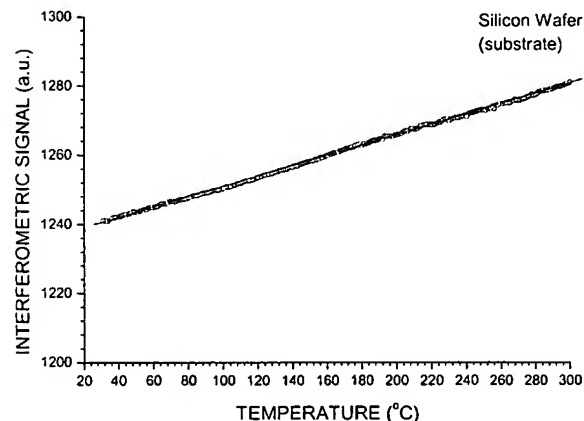


Fig. 1. The interferogram of an untreated silicon wafer (substrate).

The amplitudes of the two beams depend on the aforementioned refractive index differences. Thus, E depends strongly on the thickness and refractive index of the polymeric film and even a slight change in one or both of these parameters results in a significant change in the measuring output.

3.2. Interpretation of the interferometric signal and identification of transitions (Scheme 2)

The transitions of a polymer from the glassy to viscoelastic and/or from the solid to liquid state are accompanied by a significant increase in the free volume. Consequently, changes in the refractive index and/or thickness of the polymeric film will likely occur resulting in changes that can be monitored and recorded by a detector since the total energy (E) depends on these parameters (Eq. 1). Similar behavior is referred in the literature in the case of ellipsometry measurements for the measurement of T_g^{film} and T_m^{film} of polymers of various chemical structures.

Generally, an interferogram (interferometric signal vs. temperature) recorded by the OPTI set up, consists of linear changes of different slopes in the interference. Only during transitions when either film thickness and/or the refractive index change, a differentiation in the linear recording of the interference takes place, providing regions of inconsequence in the recorded interference prior to a transition. It is here, where glass transition or decomposition occurs and the T_g^{film} and decomposition temperature ($T_{\text{dec}}^{\text{film}}$) are calculated at the intersection point of two different linear parts. All amorphous polymers examined and presented herein behaved the same way. The signal was changed monotonically during heating whilst around glass transition and decomposition there was either a differentiation in the slope of the linearity of the interference prior to the transition or a slight curvature. The changes can in no means be attributed to the substrate because in the interferogram of the reflective substrate (silicon wafer) (Fig. 1) no irregularity in the sequence of the interference was recorded in the temperature range (30–300 °C). Although, we did not experiment (due to limitations of our experimental set up) at temperatures lower than 30 °C and higher than 300 °C, we anticipate that first and second order transitions and thermally induced decompositions that can take place in the aforementioned unexamined temperature ranges, may well be monitored and measured as well, provided the substrate does not undergo any transition. The aim of our present study was to evaluate and prove the feasibility of monitoring characteristic transitions of polymers, e.g. glass transition, melting and thermal decomposition, in thin and ultra-thin polymeric films by applying a rapid, non-invasive and high throughput technique based on the principles of the optical interferometry.

In principle, the irregularities in the interference may be attributed to first and second order transitions and thermally induced decomposition. It is well known that below T_g a

large-scale molecular movement is arrested (glassy state). Near the glass transition temperature the mobility of the macromolecular chains is a strong function of the temperature. During glass transition, big segments of the polymer's chains begin to move abandoning their previously occupied 'frozen' positions whilst in the glassy state and this is reflected to the energy at the detector. Even though this change in the interference is relatively intense in respect to the polymer mass that is creating it (we calculated that an average of 5–10 μg of the polymer sample are responsible for this change in the interference), it still remains significantly lower to that attributed to the polymer's melting, if any, and decomposition. The latter was in all cases tracked as a dramatic change in the slope of the interferometric signal and was usually recorded as a pattern of 3 subsequent lines of different slopes (Scheme 2) whereas that attributed to glass transition was always recorded as 3–5% 'progressive' change of the interference with one intersection point of a 2-line pattern (Scheme 2). Of course, this progress in the interference on the glass transition of a thin polymeric film is in close relation and dependence to the polymer specie itself. But, it is exactly this substantial difference in the recorded intensity and pattern change of the interference between that of the thermal decomposition and glass transition that helps their identification by easily distinguishing their corresponding interferometric signals.

To monitor a first order transition by applying the OPTI method we prepared thin films of the PVFHP, which is a crystalline polymer. The pattern of the interference changes on melting is distinctively different than those recorded on glass transition and thermally induced decomposition. In all the runs of the PVFHP₄₃₀ a characteristic pattern of 3 lines with significantly different slopes was recorded (Scheme 2). The two intersection points of these three lines were attributed to the beginning and completion of the melting, respectively. The percentage change of the interferometric signal on melting was recorded in all runs as an approximate 40% increase. These two characteristics (the interference pattern change along with the intensity of the signal) come to distinguish melting from both glass transition and decomposition. The fact that in the case of melting, two intersection points in a complex of three lines of different slopes are recorded, could be attributed to: (a) the substantial differentiation of the mobility of the polymer chains between the status prior and on the beginning of the melting and that upon the completion of the transition, where a dramatic increase of the free volume takes place, resulting to a substantial increase of the multiple reflections of the laser beam (dramatic change of the optical path and subsequent significant differentiation of the total energy detected) and (b) a more spectacular change of the refractive index upon comparing to that taking place on glass transition. The result is an intense and distinctive change of the interferometric signal that can easily identify first order transitions in thin polymeric films. Here, it has to be

noted that the intensity of the interferometric signal on melting is expected to be proportional to the percentage of the crystallinity of the polymeric sample. Even though we did not study the crystallization process due to limitations (no cooling device was included) of the specific experimental OPTI set up, we may well hypothesize that crystallinity will probably follow the same pattern in the interference changes. It should be anticipated though, that very low cooling rates, e.g. 1–2 $^{\circ}\text{C}/\text{min}$, must be applied for a successful monitoring and measurement of such transition.

It is not surprising the fact that the interferometric signal decreases or increases. This should not confuse the analysis since the increase or decrease in the interferometric signal depends on the film thickness and/or refractive index and both seem to change on the various transitions. The patterns of the transitions presented in Scheme 2 are purely qualitative and aim to offer some representation of the interferometric signal interpretation and the transitions identification via the OPTI method, and should be only considered as a generic guide in the interpretation of the interferogram of a thin polymeric film. Unsurprisingly, in some cases and as interferometry is governed by the film thickness, curvatures instead of sharp line intersections can be also recorded.

3.3. First and second order transitions and thermal decompositions in thin polymeric films

Commercially available polymers of known T_g s provided by the Aldrich Chemical Company (Section 2) were used in our present investigation and development of the OPTI method. Thin films of PMMA, PHEMA, PVCVA, PVACA, PVP and PVFHP in a wide variety of different film thicknesses (Table 1) were used as model polymeric samples for the development and evaluation of the OPTI method. Our study was particularly focused on the PMMA and PHEMA thin films as they are both of great importance in various modern technological applications. Therefore, extensive studies on the dependence of the glass transition on the film thickness of their corresponding thin films were carried out for both PMMA and PHEMA. As shown in Table 2, the T_g s of the polymeric films (T_g^{film}) for thicknesses over approx. 200–250 nm measured by the OPTI method, were consistent to those provided by the supplier and have been measured with conventional DSC. Certain differences observed can be attributed not only to the different nature of methodologies, the different heating rates applied, but also to the experimental character of our custom-assembled interferometer system.

Typical interferograms of PVACA₃₀₀, PVCVA₄₆₅, PVP₁₉₀, PHEMA₂₅₅ and PMMA₁₂₃₅ and PVFHP₄₃₀ thin films spin coated on bulk silicon substrates are presented in Figs. 2–5. In the present work we deliberately included interferograms of polymeric films of substantially different thicknesses to address the film thickness range the method was applied with success.

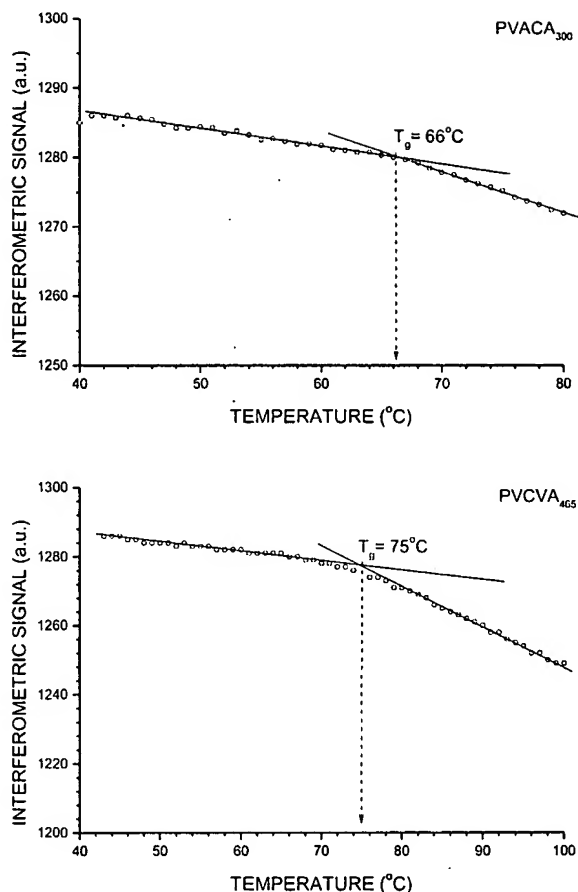
Table 2

Glass transition, melting and decomposition temperatures of the PMMA, PHEMA, PVP, PVACA, PVCVA and PVFHP thin films measured by the OPTI method

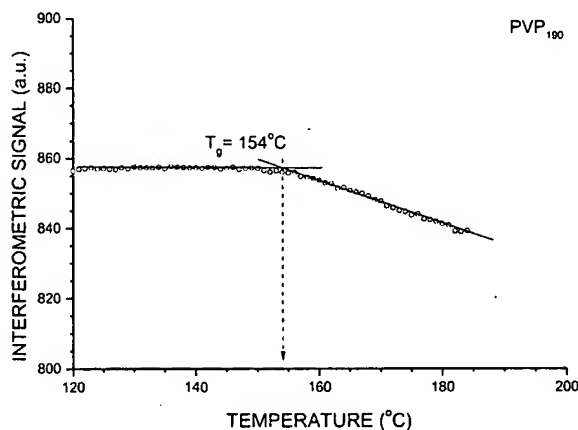
Sample film	Thickness (nm)	T_g (°C)
PMMA ₃₀	30	143
PMMA ₄₂	42	137
PMMA ₈₈	88	130
PMMA ₁₁₀	110	123
PMMA ₂₃₅	235	117
PMMA ₄₄₀	440	115
PMMA ₅₈₅	585	114
PMMA ₁₂₃₅	1235	114
PMMA _{30T}	30	143
PMMA _{440T}	440	115
PHEMA ₃₂	32	83
PHEMA ₅₅	55	76
PHEMA ₆₅	65	70
PHEMA ₁₃₅	135	64
PHEMA ₂₅₅	255	56
PHEMA ₅₈₅	585	54
PHEMA ₇₂₀	720	54
PHEMA ₁₇₃₅	1735	54
PVP ₁₉₀	190	154
PVACA ₃₀₀	300	66
PVCVA ₄₆₅	465	75
PVFHP ₄₃₀	430	Not tested

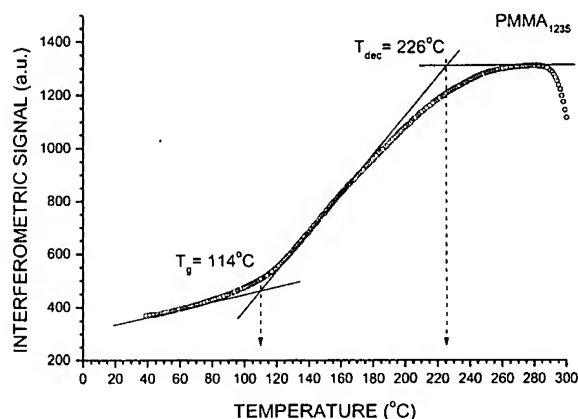
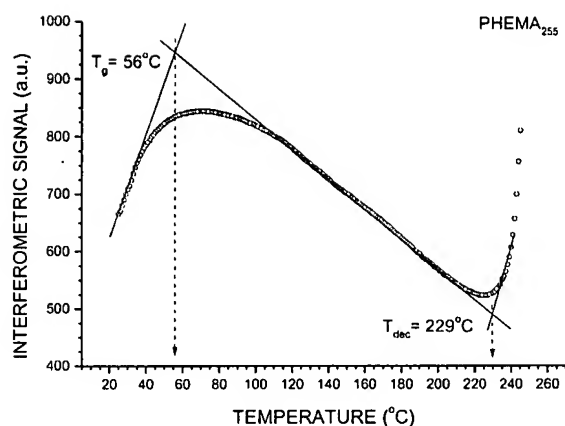
The T_g^{bulk} (DSC) values of the aforementioned polymers are: PMMA (114 °C), PHEMA (55 °C), PVP (142 °C), PVACA (61 °C), PVCVA (72 °C), PVFHP (–40 °C) and were provided by the Aldrich Chemical Company.

More particularly, in Figs. 2 and 3 are depicted the interferograms of PVACA₃₀₀, PVCVA₄₆₅ and PVP₁₉₀, where their corresponding glass transitions were recorded and their T_g s were measured at the intersection point of two distinctively different linear changes of the interferometric signal. The T_g s of PVACA₃₀₀, PVCVA₄₆₅ and PVP₁₉₀ films were found to be equal to 66, 75 and 154 °C, respectively. The T_g values of the polymers provided by the supplier were 61, 72 and 145 °C (DSC data), respectively. In the case of the PVACA and PVCVA the T_g s determined by the OPTI method were in good agreement with the T_g s determined by DSC. Upon a first hand evaluation, it seems PVP's T_g value to deviate substantially from the T_g determined by conventional DSC (Aldrich data). But, it is well known that glass transition temperatures of polymeric films with thicknesses generally lower than ~250 nm deviate substantially from the T_g values measured by DSC and PVP's film thickness was already under this crucial thickness figure. The aforementioned down limit of 250 nm in film thickness should not be considered as a standard figure and constant for all kinds of polymers as it usually depends on the chemical structure of a polymer and the affinity the macromolecular chains may develop with the reflective substrate through enhanced surface interactions when they are arranged in thin or ultra-thin films. Thus, the transitions of every thin polymeric film should be always considered individually as the ca. 250 nm of film thickness, where T_g^{film}

Fig. 2. The interferograms of PVACA₃₀₀ and PVCVA₄₆₅.

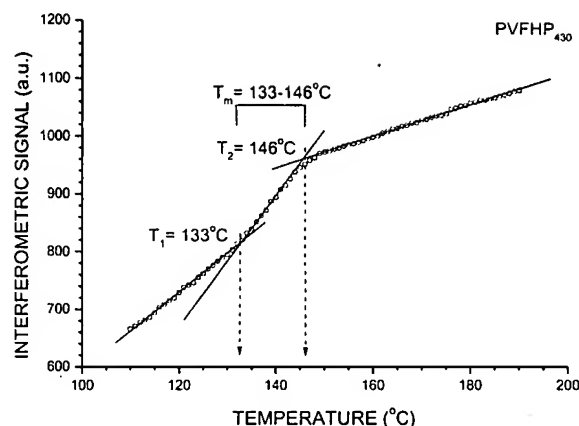
starts to deviate significantly from the T_g^{bulk} (DSC) may shift to either lower or higher figures. This was exactly the reason why we carried out a detailed study on the T_g^{film} dependence on the film's thickness and examined for this reason PHEMA and PMMA thin and ultra-thin films. In case in

Fig. 3. The interferogram of PVP₁₉₀.

Fig. 4. The interferograms of PHEMA₂₅₅ and PMMA₁₂₃₅.

which the user of the OPTI method is only interested in measuring the glass transition of a polymer and not in monitoring potential differentiations of the T_g with decreasing film thickness, then the safest approach to obtain a result comparable to that obtained by a DSC measurement, is to prepare polymeric films of preferably 0.4–0.8 μm in thickness because no differentiations between the T_g^{film} and the T_g^{bulk} , have been reported so far.

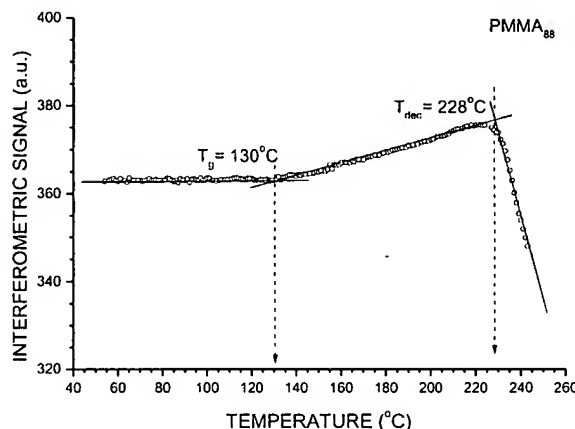
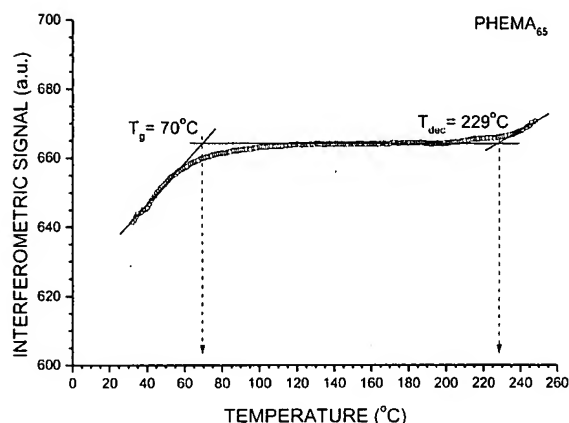
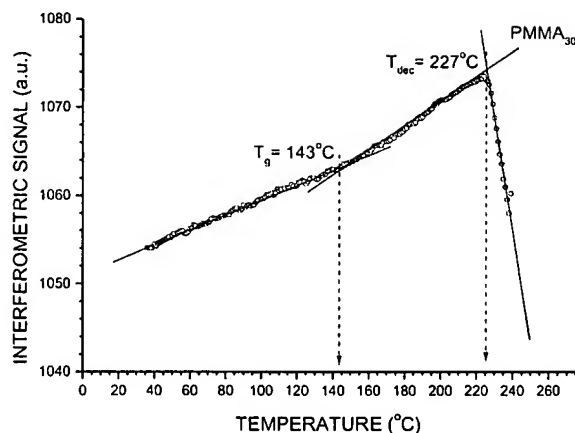
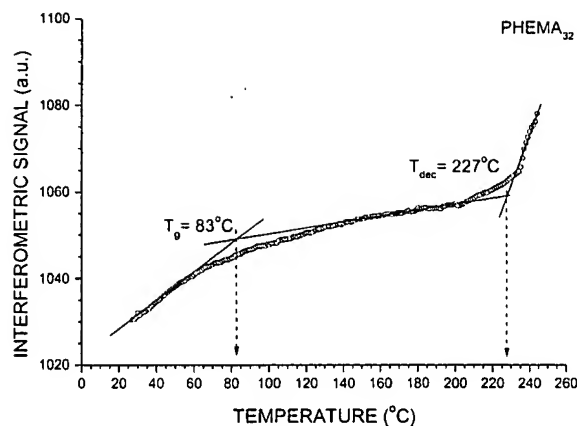
Fig. 4 depicts the interferograms of the PHEMA₂₅₅ and PMMA₁₂₃₅ films, respectively. In these interferograms both the glass transition and decomposition were monitored and their corresponding glass transition and thermal decomposition temperatures were measured according to the principles of interpretation and transitions identification mentioned here before (Scheme 2). In this case the T_g 's of both polymeric films ($T_g^{\text{filmPHEMA}} = 56^\circ\text{C}$ and $T_g^{\text{filmPMMA}} = 114^\circ\text{C}$) were in excellent agreement to that provided by the supplier (55 and 114°C , respectively). It becomes obvious, that it is feasible to monitor and measure T_g and T_{dec} upon a single run and this is quite advantageous to other similar techniques (e.g. ellipsometry) that are significantly more time demanding.

Fig. 5. The interferogram of PVFHP₄₃₀.

The crystalline PVFHP was selected in order to examine the possibility, if any, to monitor first order transitions (melting/crystallization) in thin polymeric films. Therefore, the interferometric signal of a 430 nm PVFHP film was recorded and is depicted in Fig. 5. The T_m (133– 146°C) of the PVFHP₄₃₀ that was measured according to what has been mentioned earlier (Scheme 2) was relatively in very good agreement to the data provided by the supplier and the interferometric signal recorded was substantially more intense and quite distinct to that usually recorded on glass transitions and decompositions.

A thorough investigation of the effect of film thickness on the recorded T_g^{film} values of certain thin polymeric films measured by the OPTI method was also carried out and the results are reported here after. Polymeric films of PHEMA and PMMA of various film thicknesses ranging from 30 up to 1735 nm were prepared and their T_g^{film} 's were measured from their corresponding interferograms (Table 2). Figs. 6 and 7 depict the interferograms of PHEMA₃₂ and PHEMA₆₅, as well as of PMMA₃₀ and PMMA₈₈, respectively. Again, in these interferograms was recorded not only the glass transition but the thermally induced decomposition as well. It becomes evident the significant deviation of the T_g^{film} values of both polymers' ultra-thin films from the T_g values of their corresponding polymers. The T_g^{film} values of the aforementioned PHEMA and PMMA ultra-thin films were 83, 70, 143 and 130°C , respectively, and their decomposition temperatures were measured at approximately 230°C . The interferograms of the PMMA_{30T} and PMMA_{440T} (films prepared upon spin coating of PMMA solutions in toluene) were identical to those of PMMA₃₀ and PMMA₄₄₀ that have been prepared from solutions in PGMEA (Section 2). This fact provides good evidence that at least in the case of the PMMA, the solvent did not differentiate the behavior of its macromolecular chains arranged in thin films of nanoscale thickness.

In Fig. 8 all the T_g^{film} data of PHEMA and PMMA thin films were collected and are presented in two separate

Fig. 6. The interferograms of PHEMA₃₂ and PHEMA₆₅.Fig. 7. The interferograms of PMMA₃₀ and PMMA₈₈.

diagrams aiming to elucidate the way these two polymers behave when coated in ultra-thin films. Not considerable differences were observed in the T_g values of PHEMA and PMMA films with film thicknesses higher than approx. 200–250 nm. This result is in good agreement with previously published results [11,19–21]. It becomes apparent though, that T_g^{film} of both polymeric films is increased by decreasing film thickness. Especially in sub-0.1 μm film thicknesses the increase in glass transition temperatures was significant and deviated substantially by approximately 30 °C from the T_g values of their corresponding polymers. It is well established that ultra-thin films favor polymer conformations with enhanced stereoregularity and consequently potent surface interactions take place and may govern the dynamics of phase changes. In addition, it should not be neglected the fact that in the nanoworld hydrogen bonding is magnified and thus the formation of polymers with enhanced stereoregularity is further promoted. In the case of polymers that possess chemical groups, e.g. $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, etc., an increase in the affinity between the polymeric film and the polar (SiO_x , native oxide layer) substrate, e.g. through hydrogen bonding,

should be recorded as an increase of the T_g^{film} . Thus, it seems that enhanced surface interactions of the PHEMA ultra-thin films with the substrate (silicon wafer) through hydrogen bonding is probably the dominant mechanism for the significant increase of the T_g^{film} of PHEMA's ultra-thin films. PMMA does not possess chemical groups as those mentioned here before, however, it does have polar atoms (oxygen) that again might be responsible for hydrogen bonding with the polar native SiO_x layer of the reflective silicon substrate, resulting to the recorded increase in its T_g^{film} values. The fact that PMMA thin films do not exhibit the same behavior when coated on Au substrates [22] makes us to believe that hydrogen bonding should be at least one of the responsible mechanisms for the recorded increase in glass transition temperature of PMMA's ultra-thin films. This same behavior of PMMA sub-0.2 μm films coated on untreated silicon substrates has been reported elsewhere [23] and was attributed to significant changes in the tacticity of the PMMA's polymeric chains resulting to increased T_g^{film} values. Although, further studies with possible supplementary experimental techniques and methods should likely be carried out in order to elucidate the

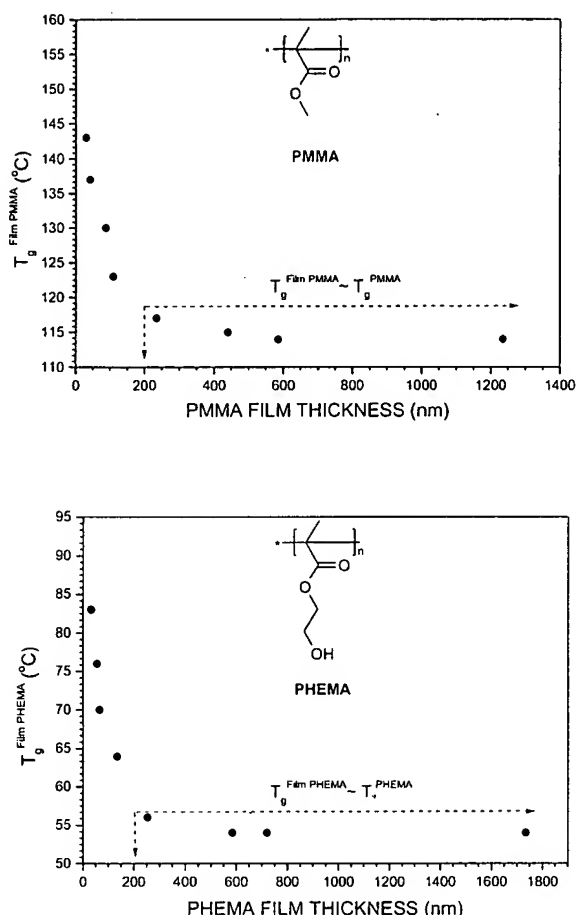


Fig. 8. Glass transition temperature dependence on film thickness for PMMA films of 30–1235 nm in thickness (top) and PHEMA films of 32–1735 nm in thickness (bottom).

PMMA's film behavior, it is believed that both the hydrogen bonding developed amongst the PMMA's oxygens and the native SiO_x substrate layer along with differentiations in the PMMA's tacticity could be probably the dominant mechanisms for explaining this result. Here, it should be stressed that the phenomenon of the increase of the glass transition temperature in films of generally sub- $0.25\ \mu\text{m}$ in thickness is not the only behavior that has been observed and it is certainly not the only to be expected. Indeed, opposite phenomena have been reported so far and come to verify that the aforementioned phenomenon is in close relation to the polymer structure [24].

The initial decomposition temperatures of the PMMA and PHEMA films measured by the OPTI method ranged from 226 up to 231 °C for both polymers and unsurprisingly were independent of their films' thicknesses. All the above observations demonstrate the importance of substrate interactions on the thermodynamic properties of confined polymer systems. The strong deviations from the bulk materials behavior observed here as well, will be a critical

issue for polymer systems which are highly interfacial in nature.

We think that the development of the OPTI method offers another useful and accurate tool in the analysis and interpretation of the behavior of polymers when these are used in thin or ultra-thin films applications. The low amount of sample needed for the analysis, the ease of sample's preparation, the relatively inexpensive equipment, the low cost of operation and maintenance, the relatively high recording speed of measurements (all transitions may be recorded in a simple run), the accuracy, and high throughput of the methodology as well as the ease of data processing, are characteristics that could successfully imply the introduction of the method in the modern analytical 'tool kit'.

Future studies will focus on the: monitoring of first and second order transitions of thin films prepared from 2-(or greater-) component polymer mixtures in solution and the correlation, if any, of the percentage of crystalline polymer's crystallinity to the actual recorded intensity and pattern of change in the interferometric signal. An investigation should be also anticipated on the possibility, if any, to monitor cross linking reaction of complex polymeric materials, e.g. photoresists, specialty coatings, etc.

4. Conclusions

The development and use of a novel, non-invasive, low cost, rapid, accurate, extremely low sample amount demanding and of high throughput analytical technique (OPTI method) that can monitor in situ, first and second order transitions and thermally induced decompositions of thin and ultra-thin polymeric films on flat reflective substrates afforded serious evidence for establishing new and straightforward approaches in the analysis of polymeric matrices of nanoscale dimensions.

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